

Effect of Surface Forces on the Gas Flow in Nanosize Capillaries

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Abstract. The flow of gas in ultrafine capillary under the action of temperature gradient is considered with allowance for the action of surface forces. It is shown that the presence of surface forces considerably increases the effect of thermal transpiration compared to the classical value determined in a free molecular regime of gas flow. The coefficient responsible for the mechanocaloric effect for the case of gas flow under the pressure gradient was also determined using Onsager relation for the kinetic coefficients calculated with account of the effect of surface forces

INTRODUCTION

Surface forces determine the velocity of thermoosmosis and the value of mechanocaloric effect upon a liquid flow in thin capillaries [1]. However, when considering the flow of rarefied gases, these forces, as a rule, are not taken into account [2-4]. This disregard is quite justified for fairly wide capillaries. However, the interest was arisen in recent years to the gas flow in nanosize capillaries whose radii are compared to the range of action of surface forces.

It was observed in some experiments [5, 6] that the values measured in ultrafine capillaries noticeably deviated from the values predicted within the Knudsen approximation. To explain observed deviations, various models accounting for rather fine effects in the gas-adsorbate-solid system were proposed [7]. At the same time, surface forces, whose role evidently rises with a decrease in capillary radius, are not considered at all in these models. Probably, this is related to the tradition established in the kinetic theory of gases: when solving problems concerning the bulk transfer processes in simple gas, the external forces appearing in Boltzmann's equation are usually excluded from the consideration using special procedures [8] so that their presence actually does not affect transfer processes. However, as we will see below, that, in the case of boundary problems of the kinetic theory of gases, one failed to realize similar procedure for the exclusion of external forces; therefore, they can noticeably affect the gas flow, particularly, in ultrafine capillaries.

In this work, we considered the flow of simple gas in ultrafine capillary in the presence of surface forces. The velocity of gas flow under the temperature gradient, and the value of mechanocaloric effect were calculated. It was shown that surface forces markedly influence the gas flow in nanosize capillaries; moreover, this effect increases with a decrease in temperature. To confirm the correctness of performed calculations, we demonstrate also the fulfillment of Onsager relations for the kinetic cross coefficients determining the velocity of gas thermal transpiration and the value of mechanocaloric effect.

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE 13 JUL 2005		2. REPORT TYPE N/A		3. DATES COVERED -	
4. TITLE AND SUBTITLE Effect of Surface Forces on the Gas Flow in Nanosize Capillaries				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Institute of Physical Chemistry, Russian Academy of Sciences, Leninski iprosect, 31, Moscow, 119991 Russia				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited					
13. SUPPLEMENTARY NOTES See also ADM001792, International Symposium on Rarefied Gas Dynamics (24th) Held in Monopoli (Bari), Italy on 10-16 July 2004.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 6	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

KINETIC EQUATION

Let us consider the flow of simple gas in the presence of pressure ∇p and temperature ∇T , gradients directed along the z axis of a capillary. We assume that the gas molecules interact with the surface of capillary walls being in the field with potential $U(r)$, where r is the distance from the capillary center. The $U(r)$ potential differs from zero in the close proximity of the surface of moderately thin capillary, i.e., at $r \approx R$ where R is the capillary radius. The state of gas is described by distribution function $f(r, z, v)$ of gas molecules over velocities v .

We assume that, as usual [2], distribution function $f(r, z, v)$ can be represented as

$$f(r, z, v) = f^{(0)}(1 + \varphi), \quad (1)$$

where φ - is the correction to local Maxwell-Boltzmann distribution $f^{(0)}$, having, in our case, the following form:

$$f^{(0)} = n(z) \left(\frac{m}{2\pi kT(z)} \right)^{3/2} \exp \left[-\frac{mv^2}{2kT(z)} - \frac{U(r)}{kT(z)} \right], \quad (2)$$

Here, n is the number of gas molecules per unit volume, m is their mass, and k is Boltzmann's constant.

For the stationary gas flow under the low pressure and temperature gradients, correction φ is found from the solution of linearized kinetic Boltzmann equation, which can be represented as

$$v_z \left(\frac{mv^2}{2kT} - \frac{5}{2} \right) \frac{\nabla T}{T} + v_z \frac{\nabla p}{p} + v_z \frac{U(r)}{kT} \frac{\nabla T}{T} + \nabla_{\mathbf{r}} \frac{d\varphi}{d\mathbf{r}} = I(\varphi), \quad (3)$$

where $I(\varphi)$ - is the linearized integral of Boltzmann collisions, \mathbf{r} is two-dimensional vector in the cross-section plane. Equation (3) differs from the equations considered earlier [2], when describing the gas flow in a capillary under the pressure and temperature gradients, by the presence of a term related to the potential of surface forces in the left-hand side of this equation.

GAS FLOW UNDER THE TEMPERATURE DIFFERENCE

As is seen from Eq. (3), surface forces affect the gas flow only in the presence of temperature gradient. We focus the main attention in this paper to this type of flow. At the same time, we also concern with the gas flow under the pressure gradient; therefore, we report the general formal solution of Eq. (3), which can be obtained by the conventional methods [2]. As a result, for the dimensionless gas velocity, we obtain the following integral equation:

$$q(r) = \frac{1}{\pi} \int_{\Sigma} d\mathbf{r}' \frac{T_0(|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} q(\mathbf{r}') - \frac{1}{2\pi} \int_{\Sigma} d\mathbf{r}' \frac{T_0(|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} \frac{\nabla p}{p} + \frac{1}{2\pi} \int_{\Sigma} d\mathbf{r}' \frac{T_0(|\mathbf{r} - \mathbf{r}'|) - T_2(|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} \frac{\nabla T}{T} - \frac{1}{2\pi} \int_{\Sigma} d\mathbf{r}' \frac{U(r')}{kT} \frac{T_0(|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} \frac{\nabla T}{T}, \quad (4)$$

where

$$q(r) = \sqrt{\frac{m}{2kT}} \frac{1}{n} \int v_z f^{(0)} \varphi dv, \\ T_n(|\mathbf{r} - \mathbf{r}'|) = \int_0^{\infty} t^n \exp \left[-\left(t^2 - \frac{|\mathbf{r} - \mathbf{r}'|}{t \text{Kn}(r')} \right) \right] dt \quad (5)$$

is the Abramovich function [2] and the integration is performed with respect to channel cross section; $\text{Kn} = \lambda(r)/R$ and $\lambda(r)$ is the local mean free path. In Eqs. (4) and (5), we took into account that, in the presence of surface forces, the mean free path (Knudsen number, Kn) depends on the distance from the wall.

Solution of Eq. (4) can be obtained in a general case (even in the absence of surface forces) only by numerical methods. We will be interested in the case of large Knudsen numbers, because it is for this regime (for nanosize capillaries) that the deviations from the Knudsen law were found in experiments. In this case, the solution of equation is obtained quite easily, if one uses the asymptotic equations for $T_n(x)$ at $\text{Kn} \rightarrow \infty$:

$$q(r) = \frac{\sqrt{\pi}}{2} R \frac{\nabla p}{p} + \frac{\sqrt{\pi}}{4} R \frac{\nabla T}{T} - \frac{1}{4\sqrt{\pi}} \int_{\Sigma} dr' \frac{U(r')}{kT} \frac{1}{|r-r'|} \frac{\nabla T}{T}. \quad (6)$$

In experiments, the gas flow rate through the capillary is measured. Dimensionless expression for the flow rate represents an integral with respect to capillary cross section on $q(r)$. It is the integral with respect to capillary cross section on the velocity. Simple calculation yields

$$Q = \frac{\pi\sqrt{\pi}}{2} R^3 \frac{\nabla p}{p} + \frac{\pi\sqrt{\pi}}{4} R^3 \frac{\nabla T}{T} - \frac{\pi\sqrt{\pi}}{2} R \int_{\Sigma} dr' \frac{U(r')}{kT} \frac{\nabla T}{T}. \quad (7)$$

Let us compare the gas flow rate due to temperature difference Q_T , and the flow rate Q_{Kn} calculated in the Knudsen approximation in the absence of surface forces. The ratio of flow rates is given by expression

$$Q_T / Q_{\text{Kn}} = 1 - \frac{2}{\pi R^2} \int_{\Sigma} dr' \frac{U(r')}{kT}. \quad (8)$$

It is seen that surface forces can both increase or decrease the flow rate compared to the Knudsen value. In this case, if the gas molecules are attracted to the wall (negative potential), the flow rate increases; when they are repulsed, the flow rate decreases.

Let us estimate the contribution of surface forces to the gas flow rate. We assume that the surface van der Waals' forces of attraction fall in accordance with the power law with an increase in the distance h from the surface of channel walls and take advantage of the following expression [9]:

$$U(h) = - \frac{\hbar \omega_0 \alpha_1 \alpha_2 q}{h^3} \quad (9)$$

where \hbar is Planck's constant; ω_0 - is the characteristic frequency of electron transitions ($\hbar \omega_0$ is approximately equal to ionization potential), α_1 and α_2 are the polarizabilities of gas and the matter of channel walls, respectively; and N is the number of atoms per unit volume of a solid.

Assuming that h is equal to 0.5 nm, the capillary radius is 10 nm and taking the corresponding values of the polarizability for argon and glass, we find the following value for the additional-to-unity coefficient of Eq. (8) at room temperature:

$$\left| \frac{2}{\pi R^2} \int_{\Sigma} dr' \frac{U(r')}{kT} \right| \approx \frac{4h}{R} \frac{\hbar \omega_0 \alpha_1 \alpha_2 q}{h^3 kT} \approx 0.3. \quad (10)$$

Even having in mind some indefiniteness of parameter h , one can easily see that accounting for the surface forces results in noticeable increase in the gas transfer through the capillary under the temperature gradient. As the temperature decreases, the effect of surface forces rises. Note also that relation (10) gives the lower estimate of correction.

THERMOMOLECULAR PRESSURE DROP

It was established long ago by the methods of kinetic theory (e.g., see [101]) that, in the limit of large Knudsen numbers for two vessels connected with a long capillary, the pressure ratio in the stationary state ($Q = 0$) coincides with the ratio determined for a small hole in thin diaphragm [11]:

$$\frac{p_1}{p_2} = \sqrt{\frac{T_1}{T_2}}, \quad (11)$$

where p_1 and p_2 are the pressures established in connecting vessels maintained at temperatures T_1 and T_2 , respectively. As was shown, equality (11) is independent of the value of the accommodation coefficient for the gas molecule momentum on the surface of channel walls. The $\Delta p = p_1 - p_2$ value is called thermomolecular pressure drop.

Relation (11) can be easily derived from Eq. (7) in the absence of surface forces. It can also be readily determined from this equation that the allowance for the surface forces changes relation (11) to:

$$\frac{p_1}{p_2} = \left(\frac{T_1}{T_2} \right)^{\beta/2}, \quad (12)$$

where $\beta \approx 1 - \frac{2}{\pi R^2} \int_{\Sigma} dr' \frac{U(r')}{kT}$.

Hence, surface forces can substantially affect the value of thermomolecular pressure drop in gases. This effect should be accounted for, in particular, when determining the so-called Eucken factor [12] for molecular gases by thermomolecular pressure drop. The use of very thin capillaries can markedly distort the experimental results.

NONEQUILIBRIUM THERMODYNAMICS OF GAS FLOW IN THE FIELD OF SURFACE FORCES

It is interesting to note that the presence of surface forces slightly modifies the expression for the entropy production in the inhomogeneous gas flowing through the capillary under the pressure and temperature gradients. Taking into account the contribution from intermolecular collisions and collisions of molecules with the surface of channel walls to the entropy production, after transformations similar to those used in [4, 13], we arrive at the following expression for the entropy production:

$$\Delta S = \langle J_m \rangle \frac{\nabla p}{T} + (\langle J_q \rangle + \langle J_m \frac{U}{kT} \rangle) \frac{\nabla T}{T^2}, \quad (13)$$

where angular brackets denote the averaging over the channel cross section; J_m and J_q are the densities of mass and heat fluxes, respectively.

Phenomenological equations of nonequilibrium thermodynamics acquire now the following form:

$$\begin{aligned}
\langle J_m \rangle &= \lambda_{11} \frac{\nabla p}{T} + \lambda_{12} \frac{\nabla T}{T^2} \\
\langle J_q \rangle + \langle J_m \frac{U}{kT} \rangle &= \lambda_{21} \frac{\nabla p}{T} + \lambda_{22} \frac{\nabla T}{T^2}
\end{aligned}
\tag{14}$$

where kinetic coefficients λ_{ij} should satisfy Onsager symmetry relation $\lambda_{12} = \lambda_{21}$. This symmetry relation can be easily proved within the brackets of kinetic theory, for example, as was done in [14]. We do not perform these calculations in this work in order to avoid complicated mathematical manipulations but consider the applicability of this relation at a qualitative level.

The presence of surface forces leads to the appearance of additional summand in the expression for the flow of matter caused by the temperature gradient [the last summand in Eq. (6)], which is proportional to the potential of interaction between the gas molecules and the surface. During the gas flow only under the pressure gradient, such a summand is absent in the kinetic equation. For this reason, there is also no corresponding contribution to the isothermal heat flux. However, the second equation of system (14) contains in its left-hand side the summand proportional to the potential of surface forces. Therefore, coefficient λ_{21} should represent the sum of two contributions, namely, one contribution from the isothermal heat flux similar to that in the Knudsen gas flowing under the pressure gradient and, the second, from the combination of the flux of matter and surface potential and similar to the contribution to the flux of matter due to temperature gradient. Thereby, the identical structure of the λ_{12} and λ_{21} coefficients is evident.

CONCLUSIONS

Note yet one important circumstance concerning the effects considered above. Earlier we took into account only purely kinetic effect resulted to the substantial change in the effect of thermal transpiration. In this case, we put aside still one more possible reason for its variation. Namely, in the presence of surface forces, the average density of gas molecules in a capillary differs from the gas density in larger vessels. In fact, we found that this effect is larger than that calculated for the "correct" average density of molecules. With respect to fluxes calculated with "incorrect" density assigned to large vessels, the allowance for surface forces leads to still larger (exponential) intensification of gas transfer due to Boltzmann factor. This component of amplification effect is calculated in a quite trivial manner; hence, we omitted this component in our analysis. Its manifestation depends on the experimental procedure. If the capillary size is determined by the isothermal gas flow rate through the capillary, the Boltzmann factor is automatically excluded from the consideration. If the capillary size is determined independently, this factor should also be accounted for.

In conclusion, note that all effects considered above do not reflect the whole set of phenomena related to the effect of surface forces on the processes of gas transport in ultrafine capillaries. Other possible effects will be considered in forthcoming publications.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 03-01-00424.

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